

**Perspectives on the Confirmation of 2,3,7,8-TCDF
for
Isotope-Dilution HRGC/HRMS Methodologies**

“How the introduction of new technologies combined with the absence of
resilience can inadvertently lead to unethical practices.”

prepared

by

Yves Tondeur, Ph.D.

03 APR 2001

Updated 02 OCT 2008

(new company name, merging several documents and inclusion of EPA letter)

On the Confirmation of 2,3,7,8-TCDF**1. Introduction**

For one particular congener, i.e., 2,3,7,8-TCDF, EPA methods on the determinations of PCDD/Fs usually require an additional analysis to be performed on a second GC column. This additional GC/MS analysis, which is performed on the same extract, has come to be known as the “confirmation” analysis. Although the selection of the “confirmation” terminology is not the best, the need for such analysis is driven by the fact that the original analysis (performed on a 60-m DB-5 column) is not capable of separating the 2,3,7,8-TCDF isomer from a number of other TCDF isomers. Thus, on the DB-5 column, the concentration for 2,3,7,8-TCDF can be biased high due to the coelution of other possible TCDF isomers. The “confirmation” analysis of 2,3,7,8-TCDF is then accomplished using a second column known as the DB-225 (30 m), which is capable of separating the 2,3,7,8-TCDF isomer from other TCDF isomers. It is worth mentioning that a “confirmed” result for 2,3,7,8-TCDF does not change the total TCDFs or the total PCDD/Fs. It will influence the TEQ calculations. EPA methods usually recommend the use of particular GC columns rather than impose particular GC columns.

2. Objective

The purpose of this communication is to present a viable alternative for the measurement of 2,3,7,8-TCDF so that it offers an accurate measurement for 2,3,7,8-TCDF that is equivalent—if not of higher reliability relative to the DB-5/DB-225 approach.

3. Benefits

In addition to providing a reliable and accurate confirmed concentration for 2,3,7,8-TCDF, the major advantages the alternative approach offers are:

- Reduced cost
- Quicker turn-around time
- Lower uncertainty associated with the concentration for 2,3,7,8-TCDF
- More reliable data for the 2,3,7,8-TCDD isomer (the compound with the highest TEF factor)
- All of the above are consistent with the PBMS orientation (e.g., Section 9.1.2 of Method 1613B or the Methods Innovation Rule for Method 8290/0023A).

4. Approach

Analytical Perspectives' approach is absolutely consistent with the PBMS concept as described in Method 1613B and the appropriate method for Method 8290/0023A under the Methods Innovation Rule. A commercially available GC column—60-m DB-5MS—is capable of achieving the needed separation for both 2,3,7,8-TCDD and 2,3,7,8-TCDF from their respective isomers. This column was not available at the time the methods were originally developed and promulgated. As part of our internal QA, Analytical Perspectives imposes more stringent requirements that must be met and adequately documented at the beginning and ending (only for BCS₃ system) of analytical sequences during which samples are analyzed. Among the most important, we have:

- The percent valley between 2,3,7,8-TCDD and its closest eluting isomers should be equal to or less than 10 percent while the valley for 2,3,7,8-TCDF should remain at or below 40 percent when an isomolar mixture containing 2,3,7,8-TCDF and its interference 2,3,4,8-TCDF—close-eluting isomer—is analyzed as part of the verification of the calibration (i.e., BCS₃ or OPR). That is, the PD and RPD requirements for 2,3,7,8-TCDF need to be met as per our SOP, in case of an OPR, Method 1613B acceptable criteria need to be met. Note that the method calls for a 25 percent valley for both congeners.
- It is worth mentioning that under the BCS₃ approach (or even the OPR system where the interferences are spiked into the QC samples as per AP's SOP), the measurement system is challenged **when and where it is needed**. This is a key element of our **enfolded performance** approach, and is certainly a very specific application of the PBMS concept. In other words, the BCS₃ (and our enhanced version of the OPR) is a QC sample that actually demonstrates performance (here the 2,3,7,8-TCDF isomer specificity) by challenging the measurement step in such a way that the normal performance indicators (e.g., the 2,3,7,8-TCDF relative response factor) remain unaffected in the presence of the challenge (e.g., presence of close-eluting isomers) relative to a situation where the performance indicator is established in the absence of the challenge (e.g., the ICAL relative response factor for 2,3,7,8-TCDF). This approach is by far superior to the existing approach of just simply relying on an arbitrarily chosen percent valley criterion.
- The alternative approach has been validated. Supportive documentation is supplied herein along with a copy of an EPA letter approving its use. Furthermore, more than 16 soil/sediment PE samples were analyzed and reported successfully using the alternative approach. Finally, participation in annual international round-robin studies since 2000 further demonstrates the validity of Analytical Perspectives' approach.

5. Comments

- The role of the **DB-225** column as a “confirmatory” tool is undeniably a necessity to offset a known deficiency of the **DB-5** column. However, when the **DB-5MS** column is used and specific performance criteria are met, the DB-225 becomes redundant.
- As we mentioned in the Introduction, a “confirmed” result for 2,3,7,8-TCDF does not change the total TCDFs or the total PCDD/Fs. Only the TEQ calculations.
- Moreover, it is customary for laboratories to use the lower of the two results between the DB-5MS and DB-225 columns. Quite often, the result from the DB-5MS is lower (again, well within the experimental error) than the DB-225 result (our RPDs between the DB-5MS and DB-225 range from -0.5 to -5 percent; see tables). Thus, the laboratory reports the 2,3,7,8-TCDF from the DB-5MS even though a DB-225 analysis was performed. Under the particular GC conditions discussed herein, the conventional “confirmation” analysis truly turns out to be a waste of time and efforts”, not mentioning this practice is **ethically questionable** (i.e., pick and chose).
- Indeed, we question the validity and ethics of an approach whereby the analyst is “selecting” the lowest result solely on the assumption of the “absence” of interferences. When two separate GC columns perform similarly with regard to 2,3,7,8-TCDF as it is the case with DB-5MS & DB-225, analyzing the same extract on each column and selecting the lowest result amounts to the unethically equivalent of analyzing the same extract on the same column several times until the lowest result is obtained. With the two columns discussed above and the requirements outlined earlier in this document, the difference between the two columns’ results for 2,3,7,8-TCDF is only a matter of

➤ **Statistics**, and

➤ The “**state**” of the instrumentation at the time the analyses are completed.

Actually, as long as the DB-5MS and DB-225 columns are considered, our experience suggests that, when the relative percent differences between the two columns are above 10 percent, it may be more indicative of instrumentation problems, tuning differences or different instruments being used rather than the presence of interferences.

- Our experience also indicates that the error bar on the DB-225 measurement is larger than the error bar on the DB-5MS measurement. This is particularly true and significant for low-level samples. The rationale is based on the fact that the DB-225 column is
 - Shorter (30 m for DB-225 instead of 60 m for DB-5MS) resulting in an unfavorable ion source pressure, and thus impacting the sensitivity,
 - Not chemically bounded (DB-225), and thus the bleeding level is higher contributing to a higher chemical noise, which adversely affects the signal-to-noise ratio.
 - A higher error bar for 2,3,7,8-TCDF derived from the DB-225 GC column analysis will affect the error bar associated with the TEQ results.
- Analytical Perspectives previously established that the 2,3,7,8-TCDF analytical results obtained on the traditional **DB-5/DB-225** (note, not DB-5MS) arrangement are equivalent to the **DB-5MS** system:

$$\text{DB-5 / DB-225} = \text{DB-5MS}$$

What follows is the supportive documentation from numerous comparisons of the two GC columns with regard to 2,3,7,8-TCDF demonstrating unequivocally the equivalency of the approaches, and in fact the superiority of the DB-5MS GC column.

The following tables were prepared by considering a large database that we divided into three categories. Namely, low-level samples presenting 2,3,7,8-TCDF at levels below Method 23 target detection limit (<50 pg per train), medium-level samples with amounts of 2,3,7,8-TCDF ranging from 50 pg to 1000 pg per train, and high-level samples where the 2,3,7,8-TCDF amounts exceed 1000 pg per train.

For each category and for the sake of this evaluation, the value obtained from the DB-225 “confirmation” analysis is considered as the “Correct Value” while the result from the alternate column (i.e., DB-5MS) is treated as the “Measured Value”.

The bias is computed for each sample entry and expressed as a percentage of the “Correct Value”. The Mean (average) and standard deviation of the mean (SDM) are displayed in the tables alongside with the “t” values (EPA Method 301 Validation). Regardless of the level category and the number of degrees for freedom, all “t” values are below the

respective critical values showing that the differences are not statistically significant and there is no need for the computation and use of a correction factor.

All raw data and other supporting documentation can be submitted at your request. Attached to this e-mail is a copy of the Excel file that was used to derive these conclusions.

Table 1: Comparison of DB-5MS and DB-225 for low-level 2,3,7,8-TCDF samples

pg 2,3,7,8-TCDF per sample		pg 2,3,7,8-TCDF per sample	
	MV = measured value	RV = real value	Bias B = 100*(MV-CV)/CV
	Alternative	Current M23	
	DB-5MS	DB-225	
Low <50 pg (TDL)	14.6	16.1	-9
	18.8	18.9	-1
	43.1	43.1	0
	34.7	35.6	-3
	38.8	41.1	-6
	16.4	16.3	1
	16.3	16.9	-4
	13.3	14.2	-6
	44.4	52.5	-15
	25.7	32.3	-20
	35.3	43.8	-19
	45.2	52.2	-13
	36	43.5	-17
	19.9	31.7	-37
	36.9	46.5	-21
	19.1	21	-9
	46.8	50.2	-7
	21.2	22.3	-5
	17.3	17.7	-2
	12.6	15.3	-18
	6.48	8.17	-21
	8.26	10.5	-21
	32	36	-11
	18.6	22.4	-17
	44.5	44.6	0
	8.37	8.99	-7
	31	33.7	-8
	32.5	38.5	-16
	25.8	28.4	-9
	44.7	47.5	-6
	37	39.9	-7
	20.3	22.3	-9
	26	27.5	-5
	18.1	20.4	-11
	17.1	20.1	-15
	15.8	19.2	-18
	14.6	16.3	-10
	13.2	15.8	-16
	12.8	15.6	-18
Aver			-11
SD			8
t			1.430

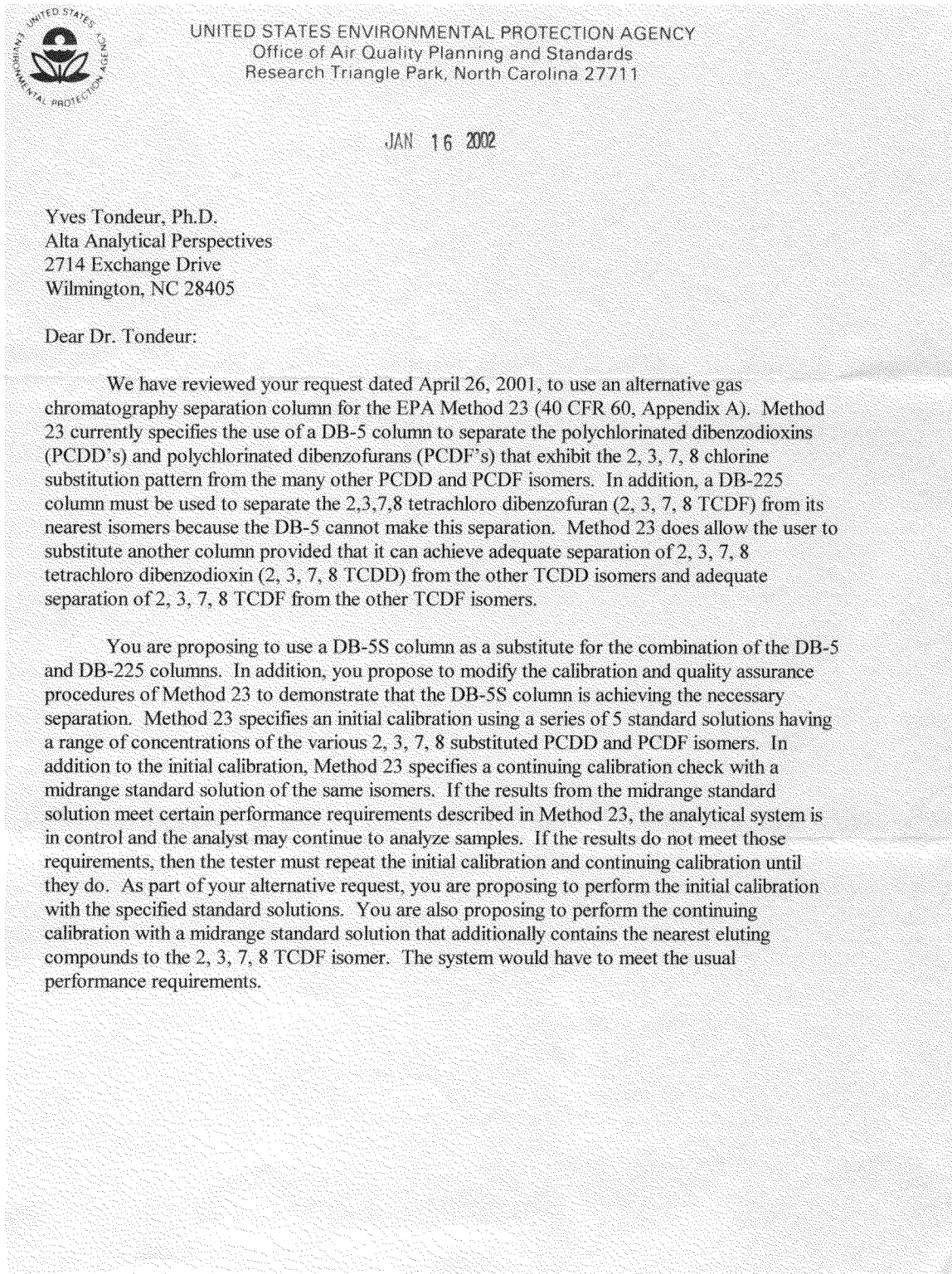
Table 2: Comparison of DB-5MS and DB-225 for medium-level 2,3,7,8-TCDF samples

pg 2,3,7,8-TCDF per sample		pg 2,3,7,8-TCDF per sample	
MV = measured value		RV = real value	
Alternative		Current M23	
DB-5MS		DB-225	
			Bias B = 100*(MV-CV)/CV
Medium 50 - 1000 pg	53.7	63.8	-16
	149	173	-14
	53.9	66	-18
	85.1	94.1	-10
	162	178	-9
	83.2	95	-12
	122	136	-10
	79.5	91.6	-13
	175	179	-2
	175	181	-3
	165	174	-5
	213	223	-4
	303	323	-6
	143	158	-9
	97.4	104	-6
	57.6	62.3	-8
	122	123.6	-1
	65.3	68.8	-5
	343	336	2
	54.4	53.1	2
	67.5	68	-1
	279	301	-7
	190	203	-6
	257	274	-6
	478	483	-1
	52.5	56.7	-7
	183	212	-14
Aver			-7
SD			5
t			1.346

Table 3: Comparison of DB-5MS and DB-225 for high-level 2,3,7,8-TCDF samples

pg 2,3,7,8-TCDF per sample		pg 2,3,7,8-TCDF per sample	
MV = measured value		RV = real value	
Alternative		Current M23	
DB-5MS		DB-225	
			Bías B = 100*(MV-CV)/CV
High >1000 pg	1130	1210	-7
	6980	7490	-7
	5090	5730	-11
	5160	5810	-11
	5440	5570	-2
	4980	4900	2
	1250	1390	-10
	1280	1390	-8
	5960	6550	-9
	36300	33200	9
	8810	8360	5
			Aver
		SD	7
		t	0.631

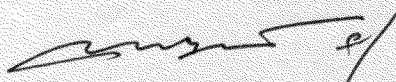
Figure 1: Copy of EPA's Letter approving the use of the DB-5MS results for 2,3,7,8-TCDF



Method 23 contains a performance specification to demonstrate that alternative column systems can achieve adequate separation. This specification uses peak resolution as a surrogate for actual separation. You are requesting the use of the new column and the modified calibration procedures as an alternative because the DB-5S column does not meet the peak resolution specification of Method 23. We have determined that you may use the proposed new column without requesting an alternative method because the quality assurance requirements you have added will demonstrate that the column is meeting the separation requirement, and therefore, meeting the peak resolution specification (which serves as a surrogate for adequate separation) is not necessary.

If you have any questions about my decision, please feel free to contact Mr. Gary McAlister at (919)-541-1062.

Sincerely



J. David Mobley Acting Director
Emissions, Monitoring, and Analysis Division

cc: Deputy Director, Office of Ecosystem Protection, Region I
Director, Division of Environmental Planning and Protection, Region II
Director, Air Protection Division, Region III
Director, Air, Pesticides, and Toxics Management Division, Region IV
Acting Director, Air and Radiation Division, Region V
Director, Multimedia Planning and Permitting Division, Region VI
Director, Air, RCRA, and Toxics Division, Region VII
Director, Air & Radiation Program, Region VIII
Director, Air Division, Region IX
Director, Office of Air, Region X
Director, Air Enforcement Division, OECA (2242A)
Director, Compliance Assurance and Media Programs Division, OECA (2223A)



[Illegible text]